CHARACTERIZATION OF WHOLE ASSEMBLY HULLS

PRODUCED BY INDUSTRIAL REPROCESSING OF LWR FUELS

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ABSTRACT

The characterization program for Obrigheim and Stade PWR hulls sampled at La Hague was conducted in the CEA hot cells (Coquenstock program operating on whole assembly hulls). A description of the appearance of these hulls, recovered on the industrial scale and after severe damage, is followed by a review of the results of the different radiochemical characterization operations (neutron emission measurements, gamma scanning, alpha and mass spectrometry after dissolution of several samples, determination of the retention of tritium and other gaseous fission products occluded in the zircalloy clads, etc.).

The alpha contamination of these hulls proved to be rather high, but it demonstrated that a large part (90 to 95%) was labile and could be removed by simple rinsing with cold 3N nitric acid. By contrast, contamination by fission products such as Cs 137, Ce 144 and Eu 154, remains high and relatively unaffected by nitric acid rinsing.

Based on the results obtained and the observations recorded, an analysis is carried out of the origins of alpha contamination of these hulls treated on an industrial scale, among which the chief source is certainly the limited effectiveness of rinsing.

INTRODUCTION

Among the solid high activity wastes produced by reprocessing, assembly hulls and ends account for the major part, and it is generally estimated that the quantities stored in the EEC by the year 2000 will amount to or even exceed 8000 tons (1). While different methods are proposed today for the packaging and storage of these wastes, the choice of one of them is still a difficult matter, due particularly to the limited knowledge available of their residual contamination by very long lived transuraniun elements.

Although a considerable body of data has been compiled on the laboratory and pilot plant scale (2,3), the data obtained on the industrial scale are rare. With the financial aid of the CEC, (4) the CEA decided to carry out an original characterization study dealing with hulls from two whole PWR assemblies sampled after chopping and dissolution in the UP2 plant at La Hague. This characterization operation, called "Operation Coquenstock", involved the following investigations (5):

1) examination of hulls and taking of representative samples by quartering,
2) measurement of neutron emissions and correlation with the residual fuel combined with the hulls,
3) determination by gamma scanning of the distribution and activities of the main beta gamma emitters in several dozen litres of hulls,
4) after the dissolution of several samples, determination of the contents of transuraniun elements, strontium 90 and alpha beta gamma activities,
5) determination of the quantities of tritium, hydrogen and gaseous or volatile FP occluded in the zircalloy clad,
6) performance of supplementary rinsing tests.

After noting the origin and the conditions for obtaining the hulls employed, the authors discuss the main results obtained. To conclude, they then examine the different sources that govern the alpha contamination of these industrial hulls.

ORIGIN AND APPEARANCE OF RECOVERED HULLS

To carry out the Coquenstock program, two separate batches of hulls were sampled in the UP2 plant at La Hague. The first, weighing 96.8 kg, was taken from a whole assembly from the West German Obrigheim PWR reactor, irradiated to 30 136 $Mwd.t^{-1}$ and discharged in June 1979. The second, which was smaller in volume, was recovered by quartering (sample weighing 22.7 kg) from a mixture of hulls from 2.5 assemblies of the West German Stade PWR reactor, irradiated to 33 153 $Mwd.t^{-1}$ and discharged in April 1980. After separation of the head and foot ends, the assemblies concerned were chopped in the HAO facility at La Hague, and the fuel was then dissolved in a 6N nitric acid solution raised to boiling for 3 hours. The dissolution liquor was then removed, and the hulls placed in the dissolver basket were rinsed by the usual procedure, with 1500 litres of 13.6N acid, and then with 800 litres of water. Hence, a total of nearly 130 litres of hulls was distributed in several containers and transferred in lead transfer casks from La Hague to the hot cells located in the Paris region.

Figure 1 shows the general appearance of the hulls after chopping up the assemblies in clusters. These hulls consist of sections, debris and fragments, whose type, shape and size vary widely and bear no resemblance to the hulls generally employed in packaging simulation experiments. As shown in Fig. 2, each section may be cylindrical (Item A), particularly long (B), shredded and cracked (C) or crushed and even blocked (D). This physical state obviously

Fig. 1. General appearance of Obrigheim hulls recovered at La Hague reprocessing plant.

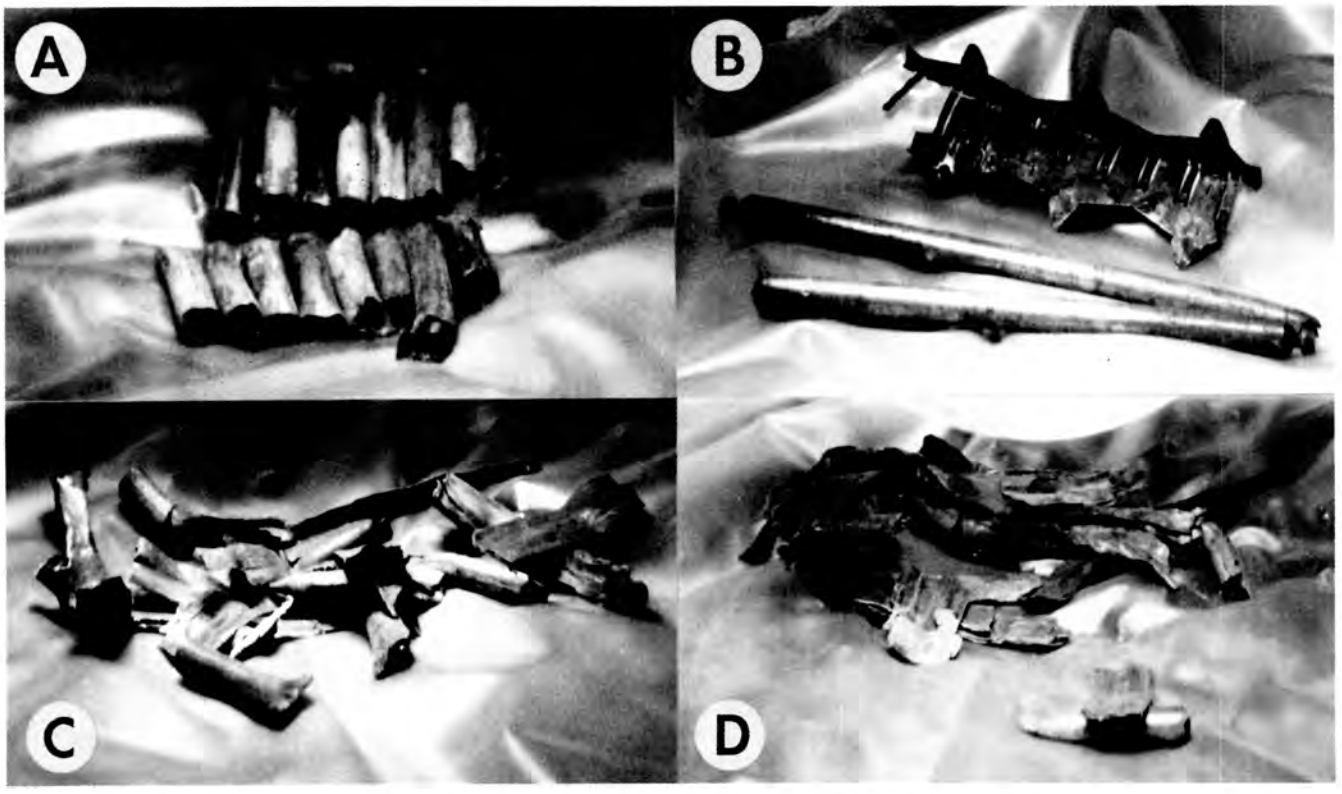

Fig. 2. Typical features of Obrigheim and Stade hulls after shearing and dissolution at La Hague plant.

favors fuel retention, essentially in the form of dissolution liquor, liable to reduce the effectiveness of rinsings.

EXPERIMENTAL RESULTS

Radiochemical analyses of the hulls were carried out by direct measurements on a fraction of 2 batches of hulls (gamma scanning) or on the whole batch (neutron emission measurements), or after dissolution. The latter case concerned more than 60 samples (weighing between 5 and 80 g), themselves taken from 2 kg samples isolated by quartering, and hence in principle, representative of each of the batches. Dissolution was carried out in nitric-hydrofluoric medium, and the following analyses were carried out on the resulting solutions:

TABLE I

Main Radiochemical Characteristics of Obrigheim and Stade Hulls
Recovered at the La Hague Reprocessing Plant (cooling time 5 years)

	Obrigheim hulls (mean values)		Stade hulls (mean values)		(%) of total amount formed during irradiation
	dissolution (a)	direct (b)	dissolution (a)	direct (b)	
Concentrations (mg.kg^{-1} of hulls)					
Uranium	(430 to 2390) $\bar{x}$ 1140	2520	(570 to 2410) $\bar{x}$ 1100	2940	0.04 - 0.1
Neptunium	(0.11 to 0.54) $\bar{x}$ 0.27		(0.17 to 0.99) $\bar{x}$ 0.36		0.03
Plutonium	(4.6 to 23.5) $\bar{x}$ 14.2	23.3	(6.4 to 27.6) $\bar{x}$ 13.1	26.3	0.05 - 0.1
Beta-gamma activities (Ci.kg^{-1} of hulls)	(c)		(c)		
FP (106 Ru + Rh	0.47	-	0.47	0.52	0.44 to 0.55
FP (134 Cs	0.16	0.13	0.19	0.16	0.16 to 0.2
FP (137 Cs	0.57	0.42	0.63	0.50	0.17 to 0.19
FP (144 Ce + Pr	0.15	-	0.17	-	0.17 to 0.19
FP (154 Eu	0.02	-	0.02	0.02	0.26 to 0.27
FP (90 Sr	0.42	-	0.48	-	0.2 to 0.21
FP (Tritium	0.82	-	0.75	-	56 to 62
FP (85 Kr	0.04	-	0.033	-	0.15 to 0.18
AP* (125 Sb	0.88	0.52	1	0.74	78.5 to 88.4
AP* (60 Co	0.13	4.05	0.21	11.2	
AP* (54 Mn	0.004	0.07	0.005	0.1	
Alpha activities (mCi.kg^{-1} of hulls)	(2.3 to 12.1) $\bar{x}$ 7.1	12 (d)	(1.4 to 26) $\bar{x}$ 9.7	20 (d)	Alpha spectrum (238 Pu 43% (241 Am 18% (244 Cm 23% (39 + 40 Pu 15% (243 Am + 242 Cm 1%

(a) Measurements after sample hull dissolution. (b) Direct measurements in hull containers.
(c) In zircalloy clad only. (d) Extrapolated value. *activation products.

1) U and Pu by mass spectrometry,
2) Pu. Am and Cm by alpha spectrometry,
3) Np by neutron activation,
4) Tritium and other gaseous FP by gaz radio-chromatography of specific dissolutions.

The main experimental results obtained with the Obrigheim and Stade hulls are summarized in Table I, and are discussed below.

Gaseous and Volatile Fission Products Occluded in Zircalloy Clads

With respect to the gaseous and volatile fission products, the fraction of tritium fixed in the zircalloy quantities formed in the reactor. The occlusion of small portions of krypton 85 (0.15 to 0.18% of the theoretical amounts) was also observed, and it was confirmed that the retention of these two nuclides in the clad normally matched the burnup, or more precisely, the axial power distribution along the fuel. In addition to these radioactive elements, non-negligible amounts of methane and hydrogen (≃120 ppm) were also detected. The hydrogen resulted from the corrosion of the zircalloy by the reactor water.

Gamma Scanning Measurements

The gamma scanning measurements are interesting because they highlight the heterogenieties in the beta gamma activities, and especially of 60 Co in the hull containers, owing to the very wide disparity of the materials making up these wastes (see Fig. 3). After 5 years of cooling, the following main gamma emitters were encountered.

- fission products, generally distributed fairly uniformly (106 Ru, 134 Cs, 137 Cs and 154 Eu) deposited during dissolution (mainly ruthenium) or which migrated to the periphery of the oxide and in the clad during irradiation,
- activation products (60 Co, 125 Sb and 54 Mn).

For the latter, the most abundant is cobalt 60, but its activity in the irradiated assemblies is largely influenced by the initial cobalt contents of the nickel alloys employed, which, in the absence of precise specifications, vary considerably from one containment to another. Note that with respect to packaging and especially shielding, it is illusory to define a mean activity for this radioisotope, which will always display a very heterogeneous distribution in the storage containers as shown by Fig. 3.

The mean FP contents in the hulls are finally fairly uniform, but higher than the plutonium contents by a factor of 2 to 35 (extreme values measured before and after supplementary rinsing, see below). Consequently, nuclides such as 137 Cs and 144 Ce cannot be considered as sensitive tracers of the residual fuel bound to the hulls. However, the higher local activities detected by gamma scanning (example of the cesium peak in Fig. 3) effectively correspond to local accumulations of fuel. As the direct FP/Pu correlation is not fully satisfactory, this technique cannot be recommended for the individual monitoring of the hulls. However, it could be used to supplement another more sensitive method, such as neutron emission measurement.

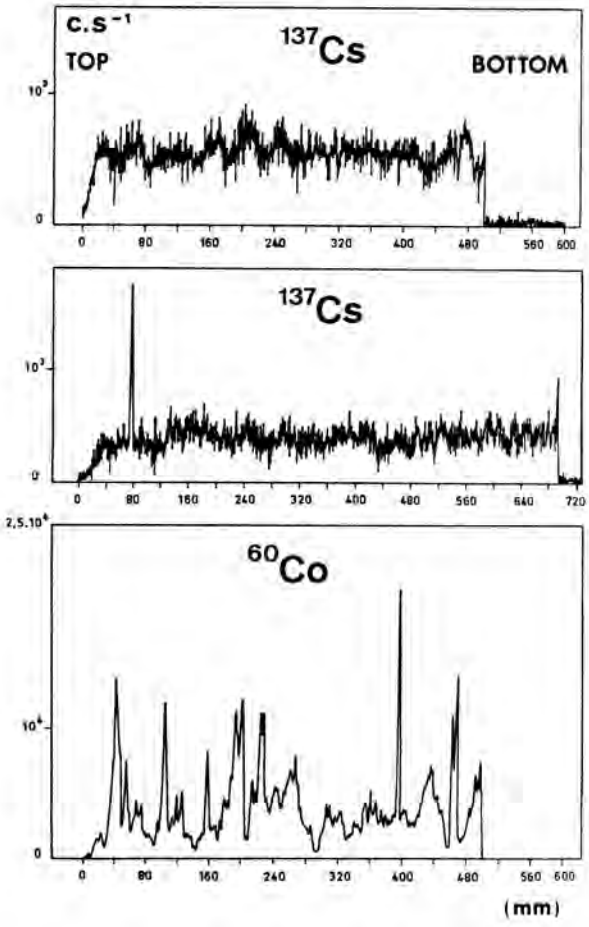

Fig. 3. Example of axial distribution for 137 Cs and 60 Co in hull containers.

Neutron Emission Measurements of Hulls

It is well known that, after 4 years of cooling, spontaneous fissions of curium 244 account for over 92% of the neutron emissions of the fuel. Assuming that this element exhibits comparable or even identical behavior to plutonium, the measurement of its neutron activity in the hulls would normally help to determine their plutonium and uranium contents. This easy-to-use technique thus appears highly attractive for the inline monitoring of hulls in reprocessing plants. However, to ensure the direct correlation of curium 244 with plutonium is satisfactory, in certain experiments, we compared the results obtained to those determined by mass spectrometry. The mean neutron emissions measured on the 2 entire batches of hulls proposed (≈100 and 25 l) are 23.3 mg plutonium per kg for Obrigheim hulls and 26.3 mg.kg^{-1} for Stade. These quantities are rather high, and present an entrainment in the hulls of about 0.1% of the plutonium formed in the reactor, or 8.15 and 9.2 g respectively per ton of initial uranium.

Table II compares the quantities of plutonium estimated from the neutron emissions with those determined by plutonium balance, for 5 samples of hulls weighing about 1 kg. Neutron counts were carried out before and after leaching of the hulls by nitric acid, and the masses of leached and residual plutonium were determined by mass spectrometry. The residual mass was determined by the dissolution of about 40 g of hulls. The table shows close agreement between these two techniques. The average differences are less than 30%, so that direct correlation of 244 Cm with unlike the FP, proves excellent, even at low concentrations (1 to 2 mg.kg^{-1}). It should be adaptable to the industrial level without any particular problem, but its accuracy is nevertheless proved by systematic prior measurements on the fuels whose residual contents in the hulls are to be determined. The sensitivity of this technique naturally depends on the noise and counting time.

Alpha Activities

The mean alpha activities calculated from the amounts of plutonium estimated by neutron measurements and from experimentally measured specific activities are rather high (Obrigheim = 12 mCi kg^{-1}, Stade = 20 mCi kg^{-1}). As for plutonium, they are higher than those determined after the dissolution of smaller samples ($\bar{x}$ = 7.1 and 9.7 mCi kg^{-1}). The main alpha emitter is plutonium 238 (40 -45% of total activity) and the local contamination of the samples is often highly variable, clearly reflecting the heterogeneities

TABLE II

Comparison of Quantities of Plutonium Determined by Neutronic Emission and by Mass Spectrometry after Dissolution of Samples

Origin of hulls	Residual plutonium measured by (mg.kg^{-1} of hulls)	
	Neutron emission	Mass spectrometry after leaching and dissolution
Obrigheim hulls		
Container 1	11.6) $\bar{x}$ 11.3±1.7	14.2 σ 4.8*
Container 2	11.0)	
Container 9		
before leaching	12.9	16.0 ± 2.1
after leaching	1.1 ± 0.16	1.1 ± 0.06
Stade hulls		
Container 1 II	14.7) $\bar{x}$ 17 ± 2.6	13.1 σ 7.2*
Container 2 II	19.3)	
Container 15 II		
before leaching	33.5 ± 5	32.1 ± 4.2
after leaching	1.3 ± 0.2	1.4 ± 0.1
Container 3 II		
before leaching	12.8 ± 1.9	12.4 ± 1.6
after leaching		1.5 ± 0.1

* σ represents the dispersion of analysed samples, the analytical inaccuracy being negligible

observed on a larger scale during neutron measurements on all the containers of the two batches of hulls. Note that the alpha contamination of pieces such as grids and guide tubes, which are not in direct contact with the oxide during irradiation, is often just as high as for the zircalloy sections.

Supplementary Hull Rinsing Tests

These rinsing or leaching tests are very important and provided an insight into the source of alpha contamination of these industrial hulls. The tests were conducted by percolation with cold 3N nitric acid, with continuous recycle for 10 to 12 hours (2 litres of acid per kg of hulls), and the operation was repeated twice for each fraction of 1 kg treated. The results of these tests can be illustrated in the typical cases shown in Figs. 4 and 5.

These leaching curves, and the activities of the radionuclides associated with them helped to show that:

- 90 to 95% of the alpha contamination of the hulls was labile,
- the fraction of FP removed (134 Cs, 137 Cs, 144 Ce and 154 Eu) during rinsings was always very limited, from 15 to 50%. After rinsing, the residual activities of these FP in the hulls still accounted for 0.15% of the quantities formed in the reactor,
- only a small fraction of the ruthenium contamination is recovered by rinsing, but this FP is known to be relatively insoluble in nitric acid,
- the second nitric rinse failed to achieve further decontamination,
- the final plutonium contents of the hulls are fairly low, 1 to 1.5 $mg.kg^{-1}$ (0.004 to 0.005% of the plutonium formed in the reactor), and appeared to vary only slightly from one fuel to another.

These leaching curves nevertheless show that the times for which the same degree of alpha decontamination was achieved were 3 to 4 times longer for the Stade hulls than for the Obrigheim hulls, due to the abnormal and accidental contamination resulting from deposits of irradiated oxide powder on the Stade hulls during the sampling operations in the La Hague plant. This explains why the decontamination rates, which are fairly high and identical for both batches during the first half-hour, then decrease for the Stade hulls and remain constant until around six hours have elapsed. This phase actually corresponds to the dissolution of the fuel powder deposited on the surface of the hulls. It is clear that this oxide would have been dissolved without any problem, had it been present during the initial dissolution carried out at boiling in the plant.

It is worth noting that, as for the Borssele and Wurgassen hulls which we characterized previously (3), the final plutonium contaminations range between 1 and 3 $mg.kg^{-1}$. These quantities appear to constitute a threshold for which the contamination mechanisms are different and also incorporate mechanisms developed during fuel irradiation (fission recoils for example), which are masked by the main contamination. The fact that the contamination of pieces such as springs, grids and guide tubes is often just as high as that of the zircalloy clads, and that this alpha contamination is fairly easily reversible, shows that it essentially results from the reprocessing conditions, and particularly the rinsing effectiveness, which is generally limited because of the static method employed, involving simple dipping.

CONCLUSIONS

In addition to the analysis of the radionuclides bound to the industrial hulls sampled in the UP 2 plant at La Hague, the characterization studies served to highlight a number of important points:

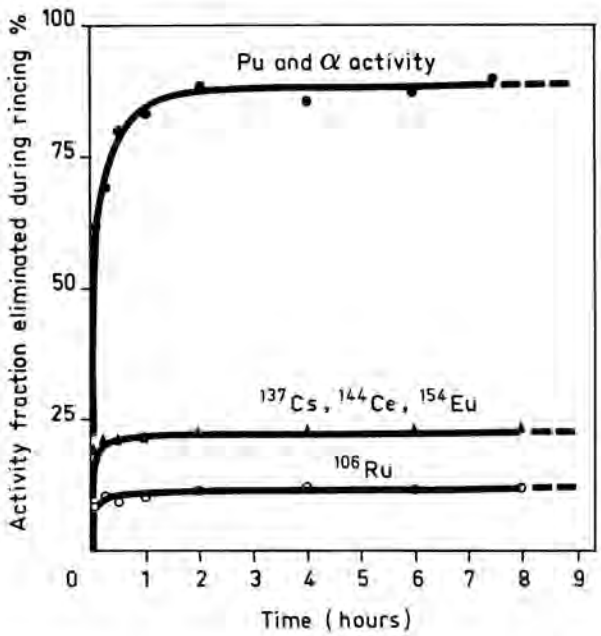

Fig. 4. Behavior of alpha and beta gamma emitters during the complementary rinsing of Obrigheim hulls by cold HNO_3.

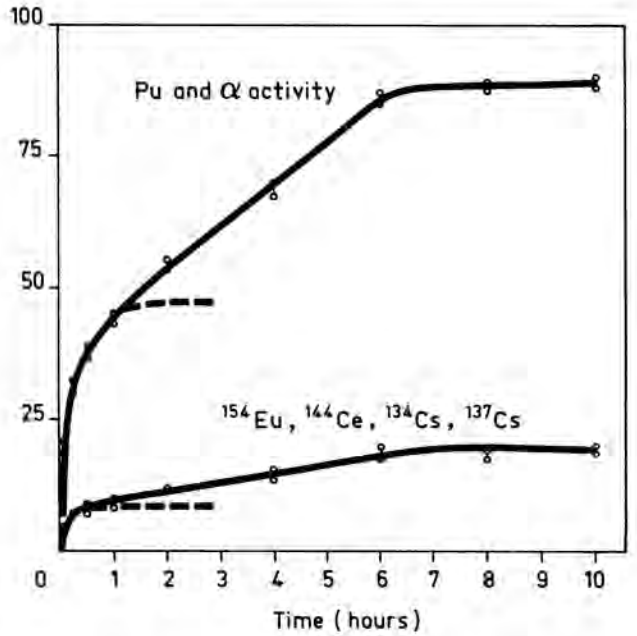

Fig. 5. Complementary rinsing of Stade hulls by cold nitric acid 3N.

1) these hulls were severely damaged, and consequently quite different from those normally used in packaging simulation experiments,
2) their cobalt 60 activity is highly variable, and this factor must be taken into account in packaging shielding calculations,
3) alpha contamination is rather high (12-20 mCi kg^{-1}), but is essentially labile and can be largely eliminated by simple rinsing,
4) unlike gamma scanning measurements, direct neutron counts help to quantify the masses of plutonium entrained with the hulls fairly accurately.

The overall results and observations compiled during Operation Coquenstock enabled us to distinguish three possible sources of alpha contamination of the hulls. The first, which is certainly the most important, includes causes of mechanical origin, associated with chopping and with the powdery state of the irradiated oxide dislodged during this operation. Among these are:

- sections blocked during chopping,
- rod ends containing oxide, whose angular position during acid attack is unfavorable and prevents the normal progress of dissolution (6),
- deposits of oxide powder during the steps after dissolution (handling of baskets, rinsings, drainage, etc.).

The second includes chemical causes:

- rinsings (method, acidity, flowrate, temperature),
- redeposition by hydrolysis, due to a local deficit of nitric acid (2),
- preferential adsorption of certain elements on the zirconia layers (particularly valency four elements).

The third, which depends on mechanisms developed during irradiation, concerns migration by thermal effect and by fission recoils, as well as the activation of zircalloy impurities (U and Th) (7).

Given the lack of experimental data, it is often difficult to determine the share of each of these processes in the total alpha contamination of the hulls. The Coquenstock experiment nevertheless seems to demonstrate that the first two are the most important. In fact, deposits of irradiated oxide powder and rinsing defects were certainly the two main causes of contamination of the Obrigheim and Stade hulls. The third process remains at a relatively low level, that we estimate at 1-1.5 mg Pu per kg, contents which may partially include the redeposition and absorption mentioned above.

Hence, the reprocessing conditions appear to be decisive for hull contamination. Thus, to reduce the alpha activity of these wastes significantly, it is important to carry out effective rinsings, and we believe that the continuous chopping, dissolution and rinsing technique to be applied in the UP3 plant (8) will help to achieve this aim. Yet the lowering of fission product contamination will always remain quite limited.

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